



Preparation and Characterization of Structurally Stable Hexagonal and Cubic Mesoporous Silica Thin Films

Ji-IN JUNG, JAE YOUNG BAE AND BYEONG-SOO BAE*

*Laboratory of Optical Materials and Coating (LOMC), Department of Materials Science and Engineering,
Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Republic of Korea*

bsbae@kaist.ac.kr

Abstract. Transparent mesostructured silica-surfactant composite films were prepared by spin coating on silicon wafers at room temperature. A cumulative heating procedure that evaporates excess solvents and decomposes surfactants produced structurally stable mesoporous silica films. The X-ray diffraction patterns of the films indicate that both hexagonal and cubic mesoporous silica films can be formed by varying the surfactant to silicon mole ratio. The hexagonal and cubic ordered structures of the calcined mesoporous silica films were confirmed by TEM. Compared with hexagonal mesoporous silica films, the cubic mesoporous silica films had lower refractive index and higher BET surface area.

Keywords: mesoporous materials, sol-gel, silica thin films, spin coating, TEM

1. Introduction

Mesoporous materials with hexagonal, cubic, or lamellar structures were invented by scientists at Mobil Corporation in 1992 [1, 2]. These materials have ordered cages or channel mesopore and high surface area. The mesoporous silica thin films are promising materials in such applications as membrane separations, chemical sensors, optical devices, and electronic devices like low- k dielectric films where powder samples cannot be easily used and a thin film is necessary [3–7]. Olson et al. reported the dispersion of a bulk silica phase into a liquid that was dip-coated onto a substrate. This resulted in a noncontinuous, nonuniform coating of colloidal particles that had been homogeneously nucleated in solution [8]. Ogawa reported the formation of lamellar and hexagonal thin films from alkoxysilane/surfactant solutions that were spin-coated onto nonporous substrates [9]. By changing the ratio of surfactant to silica precursor solutions, the silica-surfactant composite films acquire lamellar, hexagonal, or cubic mesostructures [10, 11].

The mesostructure of silica-surfactant composite films may collapse during the decomposition of the surfactant. Thus, the thermal decomposition of the surfactant in the silica-surfactant composite films is very important process in making structurally stable mesoporous silica films. Structurally stable mesoporous films yield hexagonal or cubic mesostructure after calcination.

In this study, optically transparent and crack-free mesostructured silica-surfactant composite films were synthesized by rapid solvent evaporation during spin coating process. Subjecting the silica-surfactant composite films in a heating process that progressively increases temperature produces structurally stable mesoporous silica films. Likewise, changing the ratio of surfactant to silica precursor alters the mesostructure of the mesoporous silica films. The characteristics of the mesoporous silica films with different mesostructure are investigated by XRD, TEM, N_2 sorption isotherms and ellipsometry.

2. Experimental Procedure

Tetramethylorthosilicate (TMOS, Aldrich, 98%) was hydrolyzed under acidic conditions (HCl, J.T. Baker,

*To whom all correspondence should be addressed.

36.5–38%). Methanol (CH_3OH , Merck, 99.8%) was then added into the hydrolyzed TMOS at room temperature. Finally, cetyltrimethylammonium chloride (CTACl, Aldrich, 25%) was added to achieve final reactant mole ratios of 1 TMOS : 17–18 H_2O : 0.09–0.11 HCl : 6–20 CH_3OH : 0.15–0.25 CTACl. The solution was allowed to react for another 24 hours at room temperature to achieve oligomerization. The prepared solution was then deposited on Si wafers using the spin coating method. The silica-surfactant composite thin films were pre-dried at 60°C, 130°C and 200°C for 1 hour at each stage using the increasing heat procedure to remove the solvent, water, and organic template. The pre-dried films were calcined in flowing air at 450°C for 12 hours at the rate of 1°C/min to remove the organic template thoroughly. After the surfactant was removed, the thickness of mesoporous silica films was about 500 nm and the films have no cracks in the SEM images. The average roughness of the film is estimated to be less than 2 nm over a length of 1000 nm. The calcined mesoporous films have the optical transmission through the quartz above 92%.

At each step of the heat treatment process, the as-synthesized films and the heated samples were subjected to X-ray diffraction (XRD) measurements with $\text{Cu K}\alpha$ radiation (40 kV, 80 mA) at 0.01° step width and 1s step on a Rigaku D/MAX-RC diffractometer. Infrared spectroscopy was measured by a Bruker EQUINOX55 FT-IR. A JEOL JEM-2000EX electron microscope operating at 200 kV recorded the TEM micrographs of the cross section and plane section of the calcined silica films. Cross-sectional film samples on Si wafers were prepared by placing films directly onto an epoxy resin substrate. Cross-sectional slices were cut using ultramicrotome and deposited on a copper grid. An AXIC SE500 ellipsometer quantified the refractive index and thickness of the films. N_2 adsorption isotherms were measured at 77 K using a Micromeritics ASAP 2010 analyzer.

3. Results and Discussion

XRD patterns of the mesostructured films on silicon wafers indicate that a mesostructure is formed. Figure 1 shows a gradual shift of the peak to lower d -value with increasing heating temperature. Samples heated at 200°C manifested a sharp decrease in the d -value, suggesting that the structure starts thermal condensation. Moreover, the increasing full width at half maximum (FWHM) of the peak with higher temperatures

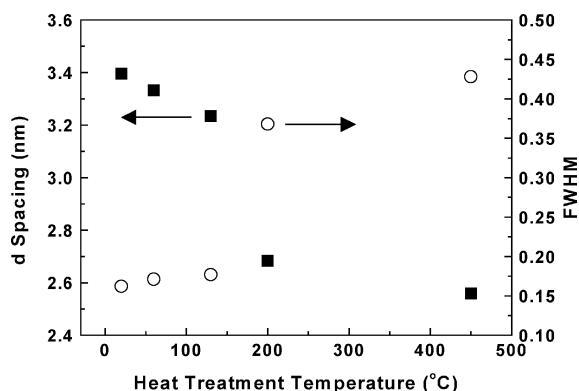


Figure 1. Thermal-induced changes of the d -spacing (■), as well as FWHM (○) of the hexagonal mesoporous silica films by the cumulative annealing procedure.

suggests less order in the temperatures up to about 200°C. The pre-dried silica-surfactant composite films at 130°C collapsed after undergoing a 450°C calcination process because of abrupt surfactant removal. Nonetheless, a 200°C heat treatment procedure gives rise to structurally stable mesoporous silica films.

The as-synthesized films were expected to have both solvent and CTACl. TGA results of the as-synthesized films show weight loss at about 60°C, 260°C, and 320°C. Each loss peak indicates desorption of solvent and CTACl and decomposition of CTACl. Figure 2 shows the FT-IR spectra of the as-synthesized and cumulatively heated samples at various temperatures. The two bands appearing at about 2856 cm^{-1} and 2926 cm^{-1} were due to the C–H stretching vibration modes coming from the surfactant in Fig. 2(a). The decreasing intensity of the two bands associated with C–H stretching vibrations with increasing heat treatment temperature suggest the gradual removal of the surfactant from the composite films. In Fig. 2(b), the other bands appearing at around 1072 and 791 cm^{-1} were associated with Si–O–Si asymmetric and symmetric bond stretching, respectively. The band at around 970 cm^{-1} was assigned to the Si–OH, whereas the same band appeared at 960 cm^{-1} in the case of the bulk alkoxide-derived silica gel [12]. The absence of C–H stretching vibration modes and silanol group for samples heated at 200°C indicates the reconstruction of the interfaces; the complete removal of the surfactant via the decomposition and dehydration of Si–OH groups. The condensation of the silanol groups was expected during the thermal treatment of the gel film.

XRD patterns of as-synthesized and calcined mesoporous silica films in Fig. 3 indicate that a mesoporous

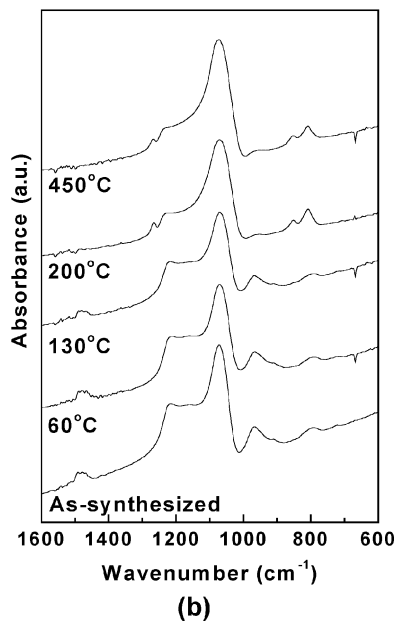
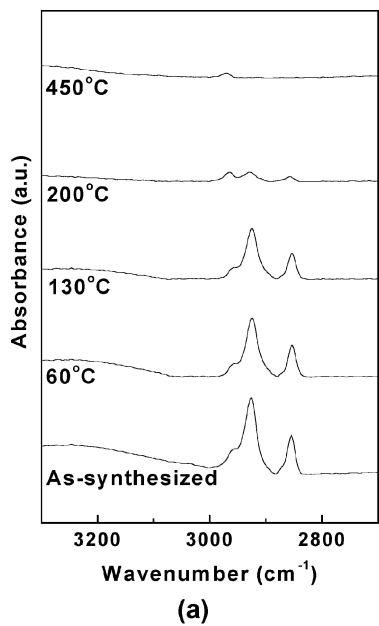


Figure 2. FT-IR spectra of (a) C—H stretching vibration modes of surfactant, and (b) silica, silanol, and methoxy modes of silica network in the hexagonal mesoporous films annealed at various temperatures.

structure is formed on the Si substrate. XRD patterns show a prominent peak at $2\theta = 2.0\text{--}4.0^\circ$ and some broad peaks at $2\theta = 4.0\text{--}7.0^\circ$ that are characteristic of hexagonal structure, which is similar to the XRD of hexagonal MCM-41 materials [1, 2] in Fig. 3(a) and

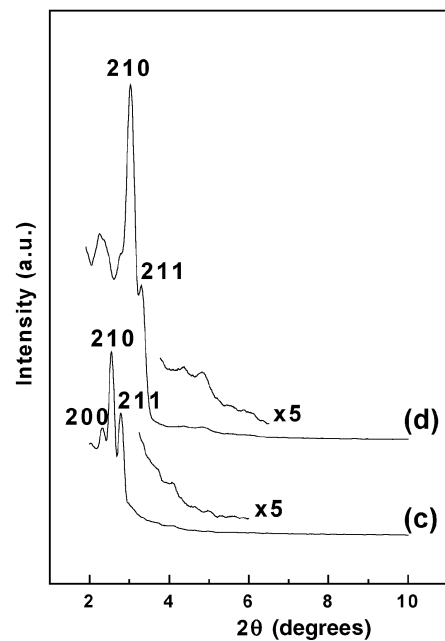
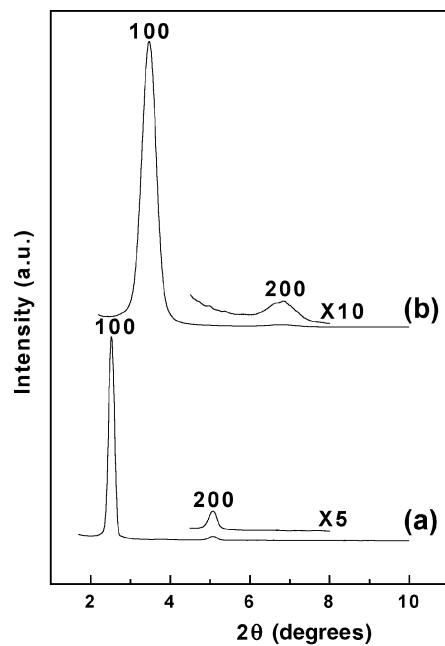


Figure 3. XRD patterns of (a) as-synthesized, (b) calcined hexagonal mesoporous silica films, (c) as-synthesized and (d) calcined cubic mesoporous silica films.

(b). Aside from preparing hexagonal mesoporous silica films, materials with cubic phase were also synthesized by changing the silicon to surfactant mole ratio in Fig. 3(c) and (d). At a Si/surfactant ratio of around 5, the predominant phase is hexagonal. At the Si/surfactant

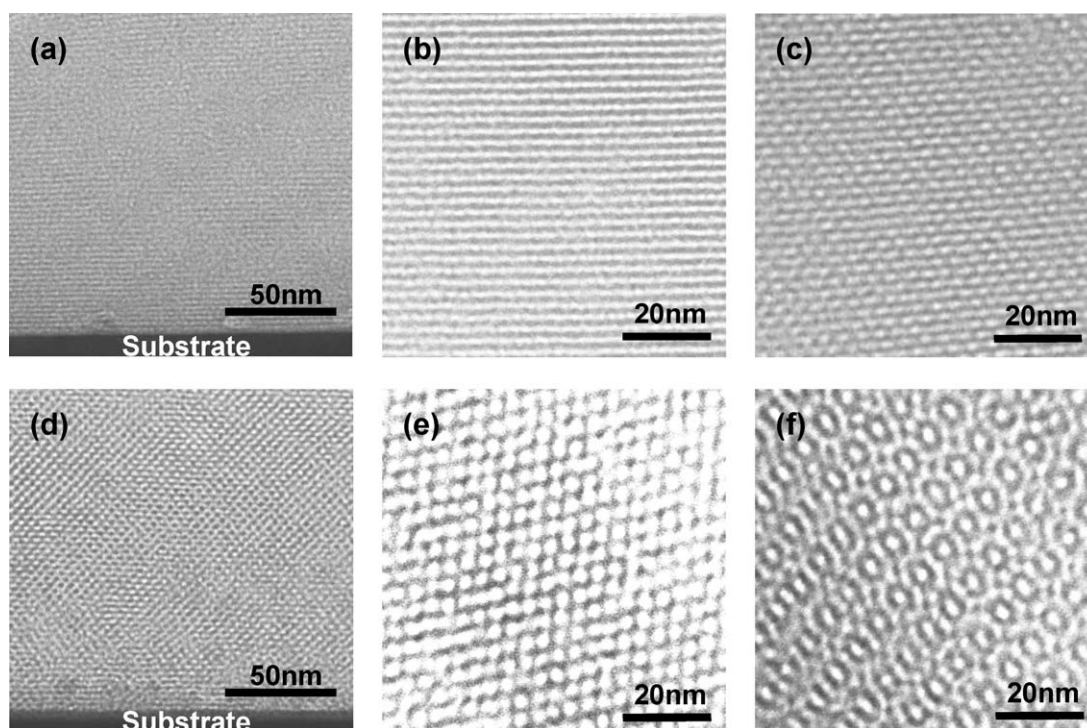


Figure 4. TEM cross-sectional images of perpendicular (a, b) and through (c) the pores of hexagonal mesoporous films and TEM images of cross-sectional view (d, e) and plane-view (f) of cubic mesoporous films.

ratio of approximately 6, a cubic phase was produced as shown in Fig. 3.

The ordered structures of the calcined mesoporous silica films clearly show a hexagonal and cubic periodicity. This was confirmed by TEM as shown in Fig. 4. TEM images of the cubic mesoporous films are also consistent with those observed for the cubic mesophase synthesized by dip-coating and subsequent calcinations [13]. These results showed that a thin film with cubic $Pm3n$ mesostructure was successfully synthesized. The refractive indices of as-synthesized silica-surfactant hexagonal and cubic composite films are about 1.475 and 1.35, respectively. The refractive indices of calcined hexagonal and cubic mesoporous silica films are about 1.283 and 1.242, respectively. The thickness of calcined mesoporous films is about 500 nm as measured using ellipsometer. The difference in the refractive indices of hexagonal and cubic mesoporous films is due to the difference in their porosity. Nitrogen sorption shows an IUPAC type IV nitrogen adsorption and desorption isotherm. Calcined hexagonal and cubic mesoporous films have a BET surface area of 834 and 920 m^2/g , respectively and an

average pore diameter of 2.1 nm. Hexagonal mesoporous films are highly oriented, but the 1-d channels run parallel to the substrate surface. This means the pores may not be accessible or may be accessible only from the edges of the coating. Cubic mesophases are useful in developing membranes and sensor products because they guarantee pore accessibility and through-film pore connectivity.

4. Conclusions

Silica-surfactant composite films with hexagonal and cubic phases are formed by controlling the concentration of the surfactant. Transparent structurally stable mesoporous silica films are formed through a heat treatment process that uses increased temperatures per process stage. Cubic mesoporous films have lower refractive index and higher surface area compared with hexagonal mesoporous silica films. Mesoporous silica films with cubic phases contain properties that are more effective in developing of applications for advanced materials.

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